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(19) (CA) **CANADIAN PATENT** (12)

(54) FIRE RETARDANT FOAM EMULSIONS AND  
FABRICS COATED WITH SUCH FOAMS

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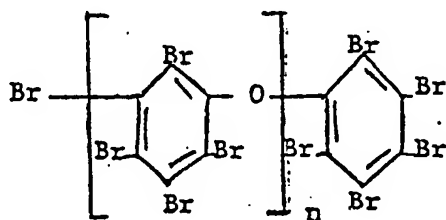
Case 1-349/CST 10

CANADA

FIRE RETARDANT FOAM EMULSIONS AND FABRICS COATED WITH  
SUCH FOAMS

Abstract of the Disclosure

A fire retardant foam emulsion comprises at least 10% by weight of coalescable emulsion copolymer particles dispersed in water thickened to a viscosity of from 500-15,000 centipoises, the emulsion being pigmented with from 10% to 35% of antimony trioxide pigment and a bromine-containing organic pigment having the formula:

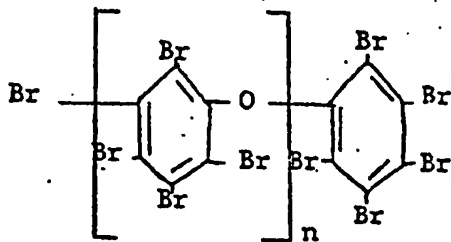


in which n is a number from 1 to 5, the equivalent ratio of antimony to bromine being in the range of 1:1 to 1:5.



## WE CLAIM:

1. A foamable aqueous emulsion composition comprising aqueous emulsion copolymer particles coalescable on air drying or baking dispersed in water providing an emulsion of foamable viscosity, a surfactant for stabilizing the emulsion and the foam produced therefrom, and a thickening agent providing a viscosity of 500 to 15 000 centipoises, said emulsion containing at least 10% by weight of copolymer solids based on the weight of the composition, said copolymer consisting essentially of monoethylenically unsaturated monomers including 0.5 to 15% by weight of monomers which provide thermosetting characteristics and monomers providing the N-methylol group, said composition being pigmented with a mixture of pigments comprising antimony trioxide and a bromine-containing organic pigment having the formula:

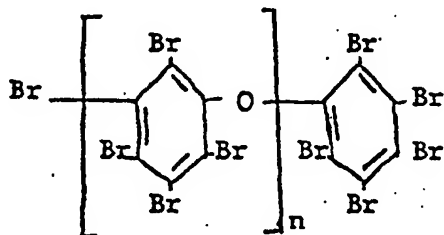


in which n is a number from 1-5, the equivalent ratio of antimony to bromine in said mixture being in the range of 1:1 to 1:5, and said mixture of antimony trioxide and bromine-containing pigment constituting from 5% to 35% of the weight of the composition.

2. A foamable emulsion composition as recited in claim 1 in which the emulsion is thickened to provide a viscosity of from 2000 to 5000 centipoises.
3. A foamable emulsion composition as recited in claim 1 in which said surfactant includes nonionic surfactant.
4. A foamable emulsion composition as recited in claim 1 in which contains at least 15% by weight of copolymer solids based on the weight of the composition.
5. A foamable emulsion composition as recited in claim 1 in which the bromine-containing organic pigment of said formula has a value for n which is 1 or 2.
6. A foamable emulsion composition as recited in claim 1 in which the bromine-containing organic is decabromodiphenyl oxide.
7. A foamable emulsion composition as recited in claim 1 in which the equivalent ratio of antimony to bromine in said mixture is about 1:3.
8. A foamable emulsion composition as recited in claim 1 in which said mixture of antimony and bromine-containing pigment constitutes from 10 to 30% of the weight of the composition.
9. A foamable aqueous emulsion composition as recited in claim 1 in which said composition further includes an aminoplast resin.

10. A foamable emulsion composition as recited in claim 1 which is pigmented white.

11. A pigmented foam comprising an aqueous emulsion comprising an aqueous medium having colloidally suspended therein coalescable particles of emulsion copolymer consisting essentially of copolymerized monoethylenically unsaturated monomers, including 0.5 to 15% by weight of monomers which provide thermosetting characteristics and monomers providing the N-methylol group, said emulsion containing a thickener providing a viscosity of from 2000 to 5000 centipoises, and a surfactant comprising nonionic surfactant for stabilizing said emulsion and said foam, said emulsion containing at least 15% by weight of copolymer solids based on the weight of the composition, said composition being pigmented with a mixture of pigments comprising antimony trioxide and a bromine-containing organic pigment having the formula:



in which n is 1 or 2, the equivalent ratio of antimony to bromine in said mixture being in the range of 1:1 to 1:5, said mixture of antimony trioxide and bromine-containing pigment constituting from 10 to 30% of the weight of the composition, and said pigmented emulsion being whipped with gas to increase its volume from about 5 to about 10 fold.

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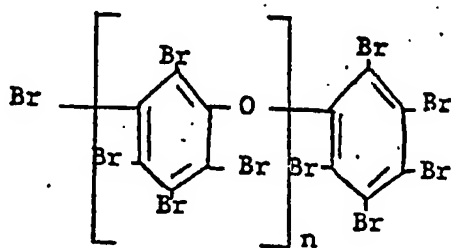
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The present invention relates to foamable aqueous emulsions and to textile fabrics having foamed layers secured thereto, the emulsions being modified so as to be fire retardant. This is a formidable task because the cellular nature of the foamed layer provides enormous surface exposure for the material which constitutes the walls of the cells, and this aggravates the combustibility of the structure.

In accordance with this invention a foamable aqueous emulsion composition is provided comprising aqueous emulsion copolymer particles coalescable on air drying or baking dispersed in water providing an emulsion of foamable viscosity, a surfactant for stabilizing the emulsion and the foam produced therefrom, and a thickening agent providing a viscosity of 500 to 15 000 centipoises, said emulsion containing at least 10% by weight of copolymer solids based on the weight of the composition, said copolymer consisting essentially of monoethylenically unsaturated monomers including 0.5 to 15% by weight of monomers which provide thermosetting characteristics and monomers providing the N-methylol group, said composition being pigmented with a mixture of pigments comprising antimony trioxide and a bromine-containing organic pigment having the formula:



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in which n is a number from 1-5, the equivalent ratio of antimony to bromine in said mixture being in the range of 1:1 to 1:5, and said mixture of antimony trioxide and bromine-containing pigment constituting from 5% to 35% of the weight of the composition.

The foamable emulsions normally have a viscosity of at least 500 centipoises up to about 15,000 centipoises. This viscosity is normally provided by incorporating a thickening agent in the emulsion.

Referring first to the aqueous emulsion copolymer particles which are employed in this invention, these are known systems and, while they are used in the present invention, the copolymers which are employed are no different than have been employed heretofore. Typical copolymers are present in the patent literature, attention being directed to U.S. Patents 3,215,647; 3,440,184; 3,527,654; 3,598,770; 3,607,341; 3,713,868; 3,714,078; and 3,732,184.

Any generally linear aqueous emulsion copolymer which will coalesce on air drying or baking and which is capable of forming a film can be employed in this invention, but it is preferred to employ a copolymer consisting essentially of mono-ethylenically unsaturated components which preferably includes a small proportion of from 0.5-15%, preferably from 2-10% by weight of monomers which provide a thermosetting cure on baking, especially those monomers which provide the N-methylol functional group. The invention will be illustrated using a copolymer of butyl acrylate and acrylonitrile in weight proportions of 80:20 which has been modified with 2.5% by weight of N-methylol acrylamide or N-methylol allyl carbamate and 2.5% of acrylamide. Copolymers of vinyl acetate with from 5-40% of ethylene are also appropriate, typically 20%

of ethylene. These may also be modified by the inclusion of monomers providing thermosetting characteristics as noted hereinbefore. Styrene-butadiene copolymers are also useful.

The aqueous emulsion in accordance with this invention is usually thickened to provide a viscosity of at least 500 up to 15,000 centipoises, the preferred viscosity being in the range of from 2000 up to about 5000 centipoises. The viscosity noted assists when the emulsion is whipped with air or other gas to provide a stable foam.

It is also necessary to employ a surfactant (emulsifier) for stability, but the utilization of surfactants for this purpose is wholly conventional. The usual surfactants may be either anionic or nonionic, or a combination of the two. The nonionic emulsifiers are illustrated by ethylene oxide adducts of long chain hydrocarbon-substituted phenols, such as nonyl phenol; the phenol being adducted to contain from 10-80 moles of ethylene oxide per mol of the phenol, preferably 20-60. Similar ethylene oxide adducts with long chain alcohols, such as dodecanol, are also suitable though less preferred. Anionic surfactants are illustrated by sodium lauryl sulfate, which may be used alone or together with the nonionics noted. Further foam stabilizers, especially ammonium stearate or sodium lauryl sulfate may be added after copolymerization has been completed.

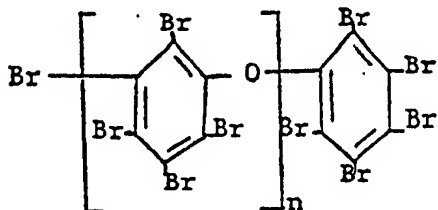
In this invention, the aqueous emulsion which is foamed should contain at least 10% by weight of copolymer solids, based on the weight of the composition, preferably at least 15%. The proportion of copolymer solids specified is necessary to provide adequate bonding of the pigment in the foam structure which is provided, and also to provide

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adequate adhesion to the fabrics which are coated.

Antimony trioxide is used as one of the pigments which is essential to the mixture of pigments which is employed, the other pigment being an organic pigment containing bromine having the formula:



in which n is a number of from 1-5. In preferred practice, n is 1, providing the compound decabromodiphenyl oxide. The corresponding brominated triphenyl oxide in which n is 2 is also useful.

The equivalent ratio of antimony to bromine in the mixture of pigments should be in the range of 1:1 to 1:5, but is preferably about 1:3 since this is the most economical utilization of the relatively expensive bromine-containing pigment.

The mixture of antimony trioxide and bromine-containing pigment should constitute from 5-35% of the weight of the composition, but is preferably in the range of 10-30% on the same basis.

In addition to the pigments noted above, other pigments may also be present such as titanium dioxide for providing increased whiteness and hide. It is also appropriate to include other pigments and fillers illustrated by calcium carbonate, talc, and clay. Dyes and colored

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pigments may also be present.

The point to be observed is that the mixture of antimony trioxide and specified bromine-containing pigment provides a foam which possesses excellent fire retardancy coupled with good color so as to permit the production of coatings of either white or some desired pastel shade.

It will be appreciated that diverse conventional materials may be added such as plasticizers, foam stabilizers, and agents to assist in the thermal cure of the emulsion copolymers particles. Aminoplast resins, especially melamine-formaldehyde condensates, are especially desirable from the standpoint of assisting in the insolubilization of the copolymer upon subsequent cure, though for many purposes, extraneous aminoplast resins would not be desired, as in the production of upholstery or mattress ticking..

The invention is illustrated in the example which follows.

#### Example

A reactor equipped with an agitator and temperature controller and jacketed for steam heating has added thereto 94.2 parts of water and 8.6 parts of hydroxy ethyl cellulose thickener, and the mixture is heated to dissolve the thickener. There are then added to the reactor 731 parts of a 45% solids aqueous emulsion copolymer in which the copolymer solids are butyl acrylate and acrylonitrile in a weight ratio of 80:20 modified to include 2.5% of N-methylol acrylamide and 2.5% of acrylamide. The copolymer is produced as described in United States Patent 3,732,184.



There is separately provided pigment slips made by grinding the pigment involved in water with the aid of a pigment dispersant as is known to the art. In this way, there is provided 238 parts of a 66% solids titanium dioxide slip, 300 parts of decabromodiphenyl oxide slip (60% solids) and dispersed with .75 parts trisodium polyphosphate, 1 part of hydroxy ethyl cellulose, .5 part ammonia, and .5 part maleic anhydride-isobutylene heteropolymer, and 113 parts of an antimony trioxide slip containing colloiddally dispersed antimony trioxide at 50% solids.

The titanium dioxide and antimony trioxide slips are commercially available materials.

The several slips noted above are added separately to the reactor with stirring to provide a homogeneous dispersion.

There are then added 15 parts of hexamethoxy methyl melamine and 27 parts of ammonium stearate foam stabilizer.

The emulsion provided as above described has a viscosity of about 1000 centipoises, and can be whipped in conventional fashion to incorporate air therein and provide a stable foam. One would generally foam the pigmented emulsion to increase its volume about 5 to about 10-fold. In this example, the final foam has a density of 120 grams per 1000 cc. volume.

Fiber glass panels were knife coated with the above foam to a depth of 50 mils (1.27 mm). These panels were dried at 180°F. for 10 minutes whereupon the parti-

ally dried coating is crushed with a roller applying 20 psi pressure and the crushed coating is cured at 300°F. for 3 minutes.

The cured coatings were white and had the appearance of ordinary foam backed drapery fabrics where the foam is pigmented white without regard for fire resistance using a simple mixture of clay and titanium dioxide. However, and unlike the conventional foam backed drapery materials which burn quite readily, even when the fabric is made of glass fibers, the coated specimens of this example are self-extinguishing as measured by standard tests in the industry.

**SUBSTITUTE**

***REMPLACEMENT***

**SECTION is not Present**

***Cette Section est Absente***